

**FINAL REPORT**

**Research Grant No. GRA-R14**

**for the period  
October 1, 1995 to August 12, 1996**

**Electrochemical Characterization  
of Semiconductor  
Materials and Structures**

**Submitted to**

**NASA Lewis Research Center**

**by**

**Cleveland State University**

***Electrical Engineering Department, Space Photovoltaic Research Center***

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## **I. Introduction**

For a period covering October 1, 1995 through August 12, 1996, the research group at CSU has conducted theoretical and experimental research on "Electrochemical Characterization of Semiconductor Materials and Structures."

The objective of this investigation was to demonstrate the applicability of electrochemical techniques for characterization of complex device structures based on InP and GaAs, Ge, InGaAs, InSb, InAs and InSb, including:

- (a) accurate EC-V net majority carrier concentration depth profiling, and
- (b) surface and bulk structural and electrical type defect densities.

Our motivation for this R&D effort was as follows: < < Advanced space solar cells and thermophotovoltaic (TPV) cells are fabricated using a large variety of III-V materials based on InP and GaAs for solar cells and low bandgap materials such as Ge, InGaAs, InAs and InSb for TPV applications. At the present time for complex device structures using these materials, however, there is no simple way to asses the quality of these structures prior to device fabrication. Therefore, process optimization is a very time consuming and a costly endeavor. > >

Completion of this R&D effort would have had unquestionable benefits for space solar cell and TPV cells, since electrochemical characterization of the above cell structures, if properly designed can provide many useful structural and electrical material information virtually at any depth inside various layers and at the interfaces. This, could have been applied for step-by-step process optimization, which could have been used for fabrication of new generation high efficiency, low cost space PV and TPV cells.

Per NASA LeRC request, on September 25, 1995 we submitted an R&D proposal, made up of four related projects of interest to NASA LeRC. To fund this effort, NASA LeRC was planning to team-up with other interested parties. The four projects and their motivation were as follows:

- PROJECT # 1:** Electrochemical Characterization of Germanium Substrates and Structures for TPV and other Device Applications.
- PROJECT # 2:** Electrochemical Characterization of InP and GaAs based Structures Grown on InP, GaAs and Si or Ge Substrates for Space Solar Cell Applications.
- PROJECT # 3:** Electrochemical Characterization of InGaAs based Structures Grown on Ge Substrates, using InP as a buffer layer, for TPV Applications.
- PROJECT # 4:** Electrochemical Characterization of InSb and InAs based Structures for TPV Applications.

Under a NASA-Lewis Research Center grant (No. GRA-R14), NASA LeRC could only secure funding for the development of Project #1, above. The funding for this project in the amount of \$9,950 was done jointly with Case Western Reserve University.

**Project #1. Electrochemical Characterization of Germanium Substrates and Structures for TPV and other Device Applications.**

### **1.1. Background**

Electrochemical C-V (EC-V) profiling<sup>1</sup> is the most often used and convenient method for accurate majority carrier concentration depth profiling of semiconductors. As seen in Table 1, not one of early developed electrolytes, recommended for EC-V profiling

of InP and GaAs based structures (such as 0.5 M HCl, Tiron, EDTA, the "pear" etch and the AT) works with all materials listed in the table. In our experience, the most common problems encountered when using these electrolytes are: (i) a poor electrolyte/semiconductor Mott-Schottky barrier (as with AT), (ii) preferential dissolution at the defect areas (as with HCl), (iii) high chemical etch rates (as with HCl, Tiron); (iv) formation of insoluble products on the surface (as with Pear etch, EDTA), (v) large parasitic capacitance components (as with HCl, Tiron and AT); (vi) a rough bottom of the etch crater (all, except EDTA for GaAs), (vii) rounding at the crater rim (as with HCl) and (viii) electrolyte seeping under the edge of the sealing rim (as with AT).

Although the FAP electrolyte is the best known to us choice for accurate profiling of InP structures, it does not work well with other III-V compounds in Table 1. To overcome this, recently we have developed a new electrolyte, which we call the UNIEL (UNiversal ELectrolyte) and which works well with all the materials in Table 1 which were made available to us. However, as with the FAP electrolyte, the presence of HF makes the UNIEL electrolyte incompatible with the electrochemical cell of Polaron EC-V profilers manufactured by BIORAD.

By slightly modifying the electrochemical cell configuration we are able to use both the FAP and UNIEL electrolytes, without destroying the callomel electrode. Recently, we have nevertheless experimenting with variations of the UNIEL electrolyte with no HF content for EC-V profiling of structures based on InP and GaAs. The best simplified combination we could so far come up with is a mixture of 0.3 M N-n-Butylpyridinium Chloride ( $C_9H_{14}ClN$ ) : 1 M  $NH_3F_2$  (4:1) electrolyte. This solution we developed using diffused junction InP structures (e.g. see Fig.1) and low and highly doped InP and GaAs wafers. Most recently, we have tried the simplified UNIEL on some of the multilayer structures made of n- and p-type InP, GaAs, InGaAs, AlGaAs, GaP and InGaAsP layers, which were made available to various electronic companies requesting assistance in EC-V profiling, and part of which we have previously used for developing the UNIEL

electrolyte<sup>7</sup>. The preliminary results show that the simplified UNIEL formulation works reasonable well with the above materials, except for the low doped InGaAsP layers, for which some of the criteria for accurate EC-V profiling are not entirely met. It also works quite well even with structures using high Al content (> 10%) AlGaP layers, for which none of the electrolytes in Table 1 seem to work due to the formation of stable residual Al oxides on the surface and with Si and Ge, in the case of structures grown on cheaper substrates.

**Table 1. Recommended electrolytes for EC-V profiling of selected III-V compound semiconductors.**

Electrolyte/ Material	HCl	Tiron	Pear etch	EDTA	AT	FAP	UNIEL
InP	x		x			x	x
GaAs		x		x	x		x
InGaAs	x			x	x		x
InGaP	x						x
GaAsP		x					x
AlGaAs		x		x	x		x
InGaAsP	x				x		x

**HCl** = 0.5 M HCl in water [2];

**Tiron** = 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt,  $C_6H_2(OH)_2(SO_3Na)_2 \cdot H_2O$  [3];

**Pear Etch** = 37% HCl-70%  $HNO_3$ -methanol (36:24:1000) [4];

**EDTA** = 0.1 M  $Na_2EDTA$  basified with ethylenediamine to pH 9.1 [5];

**Ammonium Tartrate (AT)** =  $(NH_4)_2C_4O_6$ , basified with aqueous  $NH_3$  to pH 11.5 or higher [5];

**FAP** = 48% HF-99%  $CH_3COOH$ -30%  $H_2O_2$ - $H_2O$ (10:2:1:200) [6].

UNIEL= A-B-C (1 : 4 : 1). Solution A: 48% HF : 99% CH<sub>3</sub>COOH : 85% o-H<sub>3</sub>PO<sub>4</sub> : H<sub>2</sub>O (5 : 1 : 2 : 100); Solution B: 0.1 M N-n-Butylpyridinium Chloride (C<sub>9</sub>H<sub>14</sub>ClN), and Solution C: 1 M NH<sub>3</sub>F<sub>2</sub> [7].

## References

- [1] T. Ambridge and M.M. Faktor, *J. Appl. Electrochem.*, 5, 319 (1975).
- [2] T. Ambridge and D.J. Ashen, *Electron Lett.* 15, 674 (1979).
- [3] M.M. Factor and J.L. Stevenson, *J. Electrochem. Soc.*, 125, 621 (1978).
- [4] R.T. Green, D.K. Walker and C.M. Wolfe, *J. Electrochem. Soc.*, 133(11), 2278 (1986).
- [5] PN 4200 Polaron Semiconductor Profiler, BIORAD, Instruction Manual (1988).
- [6] M.Faur, M. Faur, C.Vargas and M. Goradia, Proc.2nd IPRM Conf. UK, April 8-11, 1991, p.130.
- [7] M.Faur, M.Faur, D.J.Flood and M.Goradia, *Mat. Sci. & Eng.* B28, 361 (1994).

## 1.2. Approach:

The experimental study, which was completed by December 31, 1996 was designed to demonstrate the applicability of electrochemical characterization techniques to Ge wafers and structures. The study was based on our recently developed electrolytes for electrochemical characterization of III-V compound semiconductor materials.

The experimental research was based on:

- (a) a comprehensive electrochemical study of I-V, C-V and G-V characteristics at the liquid/semiconductor interface using the Polaron EC-V profiler;
- (b) the topography and chemical state of resulting surfaces, after dissolution the semiconductor structure to different depths, using SEM and Nomarski microscopy, Dektak profiler and EDAX and XPS spectroscopy techniques;

(c) DLTS, PLI and low frequency EG-V comparative study of surface defects.

The main parameters of interest are the variation in structural (stoichiometry, precipitates and dislocation) and electrical (carrier concentration EC-V depth profiling, recombination and trap levels) as a function of process parameters of Ge structures.

### 1.3. Electrolyte

Our results show that new formulated electrolytes (such as the "UNIEL" electrolyte, we developed for EC characterization of III-V semiconductor structures) can as well be used for accurate characterization of Ge based materials and heterostructures.

For complex multistructures for which none of the presently developed electrolyte seem to work, new electrolytes have to be developed. As known, no "wonder electrolyte" which to work equally well with all the layers can be formulated. Hence a compromised has to be made between the accuracy of profiling and the number of various layers that can be profiled with a given formulation.

The approach we have undertaken in the development of a new electrolyte for Ge structures was similar to the one we have undertaken for developing the UNIEL electrolyte for EC-V profiling of InP and GaAs based structures. The best composition of the UNIEL electrolyte we developed for accurate EC-V profiling of Ge structures is: A : B : C (1 : 8 : 2), where:

Solution A: 48% HF : 99% CH<sub>3</sub>COOH : 85% o-H<sub>3</sub>PO<sub>4</sub> : H<sub>2</sub>O (1 : 1 : 2 : 100) ;

Solution B: 0.1 M N-n-Butylpyridinium Chloride (C<sub>9</sub>H<sub>14</sub>ClN), and

Solution C: 1 M  $\text{NH}_3\text{F}_2$ .

The modified UNIEL electrolyte have been tested with very good results for EC-V profiling of a large number of  $\text{p}^+\text{nn}^+$  and  $\text{n}^+\text{pp}^+$  Ge structures fabricated in CSU by diffusion in a previous development.

#### **1.4. Deliverables.**

Using the newly developed UNIEL electrolyte described above we fully characterized a number of 14 Ge substrates and structures provided to us by NASA LeRC. A full description of the EC-V characteristics for these samples we have made available to NASA LeRC between October 1, 1995 and December 31, 1996.

Based on the above results we concluded that the EC characterization using the new formulated UNIEL electrolyte can help in step-by-step optimization of the fabrication process of Ge structures which could be used for fabrication of new generation high efficiency, low cost TPV cells, and high performance GaAs/Ge space solar cells.